PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2001-180979
(43)Date of publication of application : 03.07.2001

(51)Int.Cl. C03C 17/23
B05D 7/00
B05D 7/24

(21)Application number : 11-363915
(22)Date of filing : 22.12.1999

(71)Applicant : CENTRAL GLASS CO LTD
(72)Inventor : TANAKA KATSUTO
YAMAMOTO HIDEKI
NISHIDA YOSHIHIRO
SUGIMOTO TOSHIAKI

(54) MANUFACTURE OF GLASS COATED WITH MULTIFUNCTIONAL PHOTOCATALYTIC MEMBRANE

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a coating onto the glass substrate which expresses phtocatalytic activity and affords hydrophilicity and stainproof property effectively decomposing contaminated organic materials adhering to the surface of the glass substrate without affecting proprietary functions of reflecting heat wave and durability.
SOLUTION: This method comprises the following steps of spraying a solution comprising a titanium compound onto the surface of a glass substrate heated at the temperature of 500° C or higher, forming a primary coating comprising titanium oxide of 40 to 100 nm thickness through thermal decomposition followed by reheating at the temperature of 550 to 650° C to form a secondary coating comprising titanium oxide.

LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]
[Claim 1] The manufacture approach of the multifunctional photocatalyst film covering glass characterized by reheating the first titanium oxide coat which has 40-100nm of thickness covered on the glass substrate in temperature of 550-650 degrees C, and forming the second titanium oxide coat.
[Claim 2] The first titanium oxide coat is the manufacture approach of the multifunctional photocatalyst film covering glass according to claim 1 which carries out spray spraying of the solution which becomes the glass substrate front face heated at 500 degrees C or more from a titanium compound, and is characterized by the pyrolysis and making it come to form membranes.
[Claim 3] The manufacture approach of multifunctional photocatalyst film covering glass according to claim 1 or 2 that a light reflection factor (film surface side) is characterized by 25 - 35% and solar reflectance (film surface side) having the heat ray reflective engine performance which is 20 - 30%.

[Translation done.]

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the manufacture approach of the multifunctional photocatalyst film covering glass of high endurance of having the suitable heat ray reflex function for a structural windowpane, the windowpane for cars, etc., an antifouling function, and an improvement function in visibility by the hydrophilic property.
[0002]
[Description of the Prior Art] The heat reflective glass by the titanium oxide coat covers the heat ray in the sunrays which carry out incidence from the aperture of a building or a vehicle, and it is used for mitigation of a cooling load, or it is effective in making it hard to be visible in the interior of a room, and protecting privacy by the high reflexibility in a visible region, many things are developed until now, and it applies also for many patents. For example, it has one octylene glycol and acetylacetone in JP,54-122321,A as a chelate ligand, or the pyrolysis of the titanium compound which has at least one isopropoxy group or a butoxy radical is carried out to it on a glass front face, and the approach of forming a coat is indicated in titanium oxide.
[0003]
[Problem(s) to be Solved by the Invention] However, since a coat side is irregular compared with the usual glass front face, it can be [that the pollutant in atmospheric air tends to adhere] hard to use for the windowpane of a building etc. the sheet glass with which the titanium oxide coat indicated by said JP,54-122321,A was covered, and to take, when it constructs so that a coat side may be exposed to an outdoors side again. Moreover, not only with the glass with which the titanium oxide coat was covered but with usual glass, sealing agents, such as a silicon sealant used in case sheet glass is fixed to a window frame, may carry out degradation with the passage of time, the organic substance contained in a sealing agent may flow and fall with storm sewage, and the appearance of glass may be spoiled remarkably.
[0004]
[Means for Solving the Problem] By making this invention in view of the technical problem mentioned above, reheating the first titanium oxide coat which has 40-100nm of thickness covered on the glass substrate in temperature of 550-650 degrees C, and making the second titanium oxide coat form The multifunctional photocatalyst film covering glass which combined the antifouling property into which the contamination organic substance which is made to discover a photocatalyst activity function and adheres to a glass substrate front face is made to disassemble effectively, and a hydrophilic property is offered without spoiling the heat ray reflex function and endurance which are equipped conventionally.
[0005] That is, the manufacture approach of the multifunctional photocatalyst film covering glass of this invention is characterized by reheating the first titanium oxide coat which has 40-100nm of thickness covered on the glass substrate in temperature of 550-650 degrees C, and forming the second titanium oxide coat.
[0006] Moreover, the first titanium oxide coat carries out spray spraying of the solution which becomes the glass substrate front face heated at 500 degrees C or more from a titanium compound, and the manufacture approach of the multifunctional photocatalyst film covering glass

of this invention is characterized by the pyrolysis and making it come to form membranes.
[0007] Furthermore, as for a light reflection factor (film surface side), the manufacture approach of the multifunctional photocatalyst film covering glass of this invention is characterized by having the heat ray reflective engine performance in which 25 - 35% and solar reflectance (film surface side) are 20 - 30%.
[0008]
[Embodiment of the Invention] The manufacture approach of the multifunctional photocatalyst film covering glass of this invention can be manufactured according to the following processes. (1) 500 — degree C — more than — having heated — a glass substrate — a front face — a titanium compound — becoming — a solution — a spray — spraying — carrying out — a pyrolysis - membrane formation — carrying out — making — thickness — 40 - 100 — nm — having — primary — titanium oxide — a coat — covering — a process — (— two —) — primary — titanium oxide — a coat — 550 - 650 — degree C — temperature — reheating — things — secondary — titanium oxide — a coat — forming — a process .
[0009] As a titanium compound which can be used for this invention, there are titanium propoxy octylene glycolate, JI propoxy screw acetylacetonato titanium, titanium stearate, titanium isopropoxy octylene GURIKOKISHI diacetyl acetonate, etc. as a titanium tetrachloride and an organic titanium compound as an inorganic titanium compound. The solution which consists of these compounds can be pyrolyzed by carrying out spray spraying on the glass substrate front face heated by 500 degrees C or more mentioned later, and can form a titanium oxide coat. As the aforementioned diluent solvent, for example In addition, hydrocarbons and halogenated hydrocarbon, Making into 500 degrees C or more glass substrate temperature at the time of what does not contain moisture, such as alcohols, ether, ketones, ester, and fatty acids, forming said first desirable titanium oxide coat If it is less than 500 degrees C in substrate temperature, while the pyrolysis of an organic titanium compound will not happen efficiently, but becoming a coat containing undecomposed residue and reducing bond strength and an appearance remarkably, it is for a photocatalyst activity function and a heat ray reflex function also falling. In addition, substrate temperature has the more desirable range of 530-630 degrees C, and spoils [when it is 630 degrees C or more, deformation of a glass substrate may take place, and / remarkably] an appearance in image distortion etc. and is not desirable.
[0010] Next, the glass substrate with which the first titanium oxide film was covered is reheated in temperature of 550-650 degrees C, and the second crystalline high titanium oxide coat is made to form more. It is because the crystalline fall of the titanium-oxide coat by the elution of the alkali component contained in a glass substrate or the transition to the rutile form crystal of the anatase form crystal of titanium oxide takes place in the case of the temperature which sufficient photocatalyst activity function does not take place since the crystallinity of the titanium oxide coat formed as it is less than 550 degrees C in temperature does not become high, and exceeds 650 degrees C and sufficient photocatalyst activity function stops being discovered. In addition, although it does not limit especially as the holding time of reheating, for 5 - 15 minutes is more preferably good more than for 5 minutes. Even if crystallinity does not increase but it exceeds for 15 minutes in case of under for 5 minutes, crystallinity does not increase any more, or productivity worsens.
[0011] The thickness of the titanium oxide coat obtained by this invention Even if it reheats at the aforementioned temperature of 550-650 degrees C with it being required to be 40-100nm, and it being less than 40nm thickness, the crystallinity of titanium oxide does not increase, although a photocatalyst activity function will increase if a heat ray reflex function also falls and 100nm thickness is exceeded, while sufficient photocatalyst activity function is not discovered - - the excitation purity of a reflected color — high — becoming — the interference color of a chromatic color — appearing — an exterior — it is not desirable. Moreover, the light solar radiation reflective engine performance falls.
[0012] The second crystalline high titanium oxide coat obtained by the above reheating methods Even when the hydrophilic property will be maintained by the front face of this coat and dirt, such as exhaust gas and dust, adheres temporarily, while a part for organic is decomposed by the photocatalyst effectiveness Since this coat front face is a hydrophilic property, by rain or

pouring water artificially, water enters between a coat front face and dirt, and dirt floats, and flows and comes off.
[0013] As for the photocatalyst coat covering glass obtained by the approach of this invention, the variation of peak intensity have further the high endurance which maintained the balance which solar-radiation ******** (film-surface side) combine with ten or more outstanding antifouling property in evaluation of the outstanding hydrophilic property to which the contact angle seven days after setting to the evaluation of hydrophilic maintenance nature mentioned later maintained 30 degrees or more, and photocatalyst activity.
[0014] In addition, the photocatalyst coat covering glass which has the second crystalline high titanium oxide coat obtained by this invention When the ultraviolet rays included in sunlight, a fluorescent lamp, etc. are irradiated, while the operation (called an oxidative degradation mold reaction) which disassembles the organic substance which adhered to this coat front face according to the photocatalyst effectiveness, and maintains the front face of a coat at clarification is shown Hydrophilization (called a super-hydrophilic-property mold reaction) also of the front face of the titanium oxide crystal itself is carried out, and the variation of peak intensity has ten or more outstanding antifouling property in evaluation of the outstanding hydrophilic property to which the contact angle seven days after setting to evaluation of the hydrophilic maintenance nature shown in the example mentioned later maintained 30 degrees or more, and photocatalyst activity. In the case of the coat of the crystalline titanium oxide simple substance which has the photocatalyst operation which does not carry out reheating of a conventional method, while ultraviolet rays are irradiated, a photocatalyst operation is active, but Although it will return to the hydrophobicity of titanium oxide original comparatively for a short time if subsequent ultraviolet rays are intercepted even if hydrophilization is once carried out by UV irradiation, once ultraviolet rays are no longer irradiated The titanium oxide coat obtained by the approach of this invention has the description which has the engine performance which maintains a hydrophilic property in a long period of time, whether ultraviolet rays are intercepted or ultraviolet-rays reinforcement becomes a weak situation. Furthermore, it has the high endurance in which the photocatalyst coat covering glass obtained by the approach of this invention maintained balance by various functions which solar reflectance (film surface side) also has 20 - 30% of outstanding heat ray reflective engine performance, and also have the above-mentioned hydrophilic property and antifouling property.
[0015]
[Example] Hereafter, an example explains this invention concretely. However, this invention is not limited by these examples. In addition, the following evaluation was performed about the obtained sample supposing the antifouling aperture material used for sheathing, such as a building. In addition, abrasion resistance, acid resistance, and alkali resistance were evaluated based on A of JIS-R -3221 (heat reflective glass). An evaluation result is shown in Table 1.
[0016] (The evaluation approach)
** Abrasion resistance JIS R Based on the wear-resistant test method given in 3221, wear wheel CS-10F and load 500gf estimated the haze value by the Taber's abrasion resistance test. The early haze value H0, the haze value H100 of 100 times after, and the haze value of 200 times after was [H200] H0 <=H100 <=H200, and evaluation considered the case where haze variation **H of the first stage and 200 times after (**H=H200-H0) was **H<=4% as success (O), and made rejection (x) H100>H200 or a **H>4% thing.
[0017] ** acid resistance JIS R the hydrochloric acid of 1 convention kept at 23 degrees C **2 degrees C based on the acid-proof test method given in 3221 — after 24-hour immersion and a stream — it wiped away and dried in flannel in inside, and the appearance was evaluated. Evaluation considered the case where there was no remarkable appearance change as success (O), and when remarkable discoloration or a remarkable blemish entered, that in which the film exfoliated was taken as rejection (x).
[0018] ** Alkali-proof JIS R Alkali-proof test method given in 3221, the sodium-hydroxide solution of 1 convention kept at 23 degrees C **2 degrees C — after 24-hour immersion and a stream — it wiped away and dried in flannel in inside, and the appearance was evaluated. Evaluation considered the case where there was no remarkable appearance change as success

(O), and when remarkable discoloration or a remarkable blemish entered, that in which the film exfoliated was taken as rejection (x).
[0019] ** It is whenever [disassembly / of stearin acid] and the photocatalyst activity of the capacity which disassembles the dirt with which the photocatalyst activity front face was stained was evaluated. The evaluation approach is Paragon. 1000 (FT-IR made from Perkin-Elmer a spectrum equipment) is used. The peak intensity (absorbance A) resulting from the C-H stretching vibration of the stearin acid which appears from 2910cm-1 to 2920cm-1 After [A1] irradiating A0 and ultraviolet rays stearin acid spreading before Ab for 1 hour at the time of stearin acid spreading, it asks, respectively. Variation of peak intensity: |(A0-Ab) -(A1-Ab)| x1000 were computed, and it considered as whenever [disassembly / of stearin acid] (photocatalyst activity becomes high, so that whenever [stearin acid decomposition] is large).
[0020] In addition, spreading to the sample of stearin acid was immersed in the 3wt% stearin acid-ethanol solution in the sample, and was performed by pulling up by 8 mm/sec. In the source of ultraviolet rays, ultraviolet-rays reinforcement on the front face of a sample was made into 4 mW/cm2 (365nm) using black light floor line15BLB (product made from Toshiba Electrical and electric equipment). Evaluation considered the case where the variation of said peak intensity was ten or more as success, and made less than ten the rejection.
[0021] ** Also as for a hydrophilic property being maintained to some extent, the front face by which hydrophilization was once carried out in addition to photocatalyst activity was important for hydrophilic maintenance nature antifouling property, and the contact angle over water after leaving it in the laboratory under the environment below ultraviolet-rays on-the-strength 1 microwatt/cm 2 (365nm) estimated hydrophilic maintenance nature for seven days after sample production. The contact angle theta of seven days after considered theta<=30 degrees as success (O), and evaluation showed theta> 30 degrees by rejection (x).
[0022] (Example 1) As an organic titanium compound, 2.0g, 2, and 4 2,4-pentanedione (product made from KISHIDA Chemistry) was mixed for 33.2g, 2 ethyl 1, and 3 hexandiol (Tokyo formation Make), 61.6g was mixed for 3.2g and dichloromethane (Tokuyama make), JI propoxy screw acetylacetonato titanium (Nippon Soda Co., Ltd. make) was stirred enough, and coating liquid was obtained. Next, after having made it stay for 8 minutes into the electric furnace set as 600 degrees C, having picked out the glass plate from the electric furnace, carrying out [having used the float glass plate (soda lime silicate glass) with a thickness of 6mm as the substrate by often washed 300mmx300mm,] 30g spray of the coating liquid immediately and carrying out a pyrolysis on a glass substrate front face, it once cooled to the room temperature and the uniform titanium oxide coat was obtained. When the refractive index of the obtained film was measured by the ellipsomter (DVA[by Mizojiri Optical Co., Ltd.]-38-smooth S form), it was 2.30, and the thickness similarly measured by the ellipsomter was 67nm. Moreover, the reflection by the side of a film surface was measured with the spectrophotometer (Uby Hitachi, Ltd.4000 mold), and the solar reflectance of the light reflection factor based on JIS-R-3018 was 27.2% at 31.7%. Next, the crystalline titanium oxide film was obtained by putting the titanium oxide coat covering glass into the muffle electric furnace FP41 mold (product made from Yamato Science) set as 600 degrees C for 15 minutes, and carrying out reheating processing. The crystal of the obtained titanium oxide was a crystalline high anatase form crystal.
[0023] As a result of the approach of showing the obtained glass with the photocatalyst film above estimating, as shown in Table 1, it was what photocatalyst activity is as large as 14 degrees, and the sample is good, and is 25 degrees also about hydrophilic maintenance nature, and has sufficient high endurance even if it uses it for the aperture material (a film side outdoor side) of a building. In addition, the refractive index of the photocatalyst film after reheating, thickness, a light reflection factor, and solar reflectance were with the numeric value before reheating. the same glass substrate which does not have a coat as a reference — when the outdoor exposure of the independent sample was actually carried out, dirt was attached and condition was evaluated, compared with the glass substrate to which a coat is not attached, it was markedly alike, and has checked that there was little dirt.
[0024]
[Table 1]

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	○	○	○	14	[illegible]	[illegible]
[illegible]	○	○	○	[illegible]	[illegible]	[illegible]
[illegible]	○	○	○	11	[illegible]	[illegible]
[illegible]	○	○	○	[illegible]	[illegible]	[illegible]
[illegible]	○	○	○	[illegible]	[illegible]	[illegible]
[illegible]	○	○	○	[illegible]	[illegible]	[illegible]
[illegible]	○	○	○	1	[illegible]	[illegible]

[0025] (Example 2) As an organic titanium compound, 33.2g was mixed for JI propoxy screw acetylacetonato titanium (Nippon Soda Co., Ltd. make), 66.8g was mixed for dichloromethane (Tokuyama make), it stirred enough, and coating liquid was obtained. Next, after carrying out 20g spray of the coating liquid like the example 1 and carrying out a pyrolysis on a glass plate, it cooled and the uniform titanium oxide coat was obtained. The refractive index of the obtained film was 2.16 and thickness was 67nm. The light reflection factor was 28.9% and solar reflectance was 24.4%. Next, reheating processing of the glass plate with a titanium oxide coat was carried out like the example 1, and the second crystalline good titanium oxide coat was obtained. As a result of the approach of showing the obtained glass with the photocatalyst film above estimating, the result of having excelled like the example 1 was obtained.
[0026] (Example 3) After having made it stay for 8 minutes into the electric furnace set as 630 degrees C with the same coating liquid as an example 1, having picked out the glass plate from the electric furnace, carrying out 25g spray of the coating liquid immediately and carrying out a pyrolysis on a glass plate, it cooled and the uniform titanium oxide coat was obtained. The refractive index of the obtained film was 2.28 and thickness was 64nm. The light reflection factor was 32.1% and solar reflectance was 27.1%. Next, reheating processing of the glass plate with a titanium oxide coat was carried out like the example 1, and the crystalline good titanium oxide coat was obtained. As a result of the approach of showing the obtained glass with the photocatalyst film above estimating, the result of having excelled like the example 1 was obtained.
[0027] (Example 1 of a comparison) After having made it stay for 8 minutes into the electric furnace set as 450 degrees C with the same coating liquid as an example 1, having picked out the glass substrate from the electric furnace, carrying out 40g spray of the coating liquid immediately and carrying out a pyrolysis on a glass substrate, it cooled and the uniform titanium oxide coat was obtained. The refractive index of the obtained film was 1.80 and thickness was 16nm. The light reflection factor was 9.3% and solar reflectance was 5.7%. Next, reheat processing of the glass plate with a titanium oxide coat was carried out like the example 1. As a result of the approach of showing the obtained glass with the photocatalyst film above estimating, as shown in Table 1, there were not 0 degree and activity, and they were as large as about 60 degrees, and photocatalyst activity had a problem in endurance, for using it as aperture material (a film side outdoor side) of a building. [of hydrophilic maintenance nature]
[0028] (Example 2 of a comparison) Only reheat processing was excluded about the glass plate with a titanium oxide coat of an example 2. As a result of the approach of showing the obtained glass with the photocatalyst film above estimating, as shown in Table 1, for 0 degree and activity do not have photocatalyst activity, and it is as large as about 58 degrees and using a sample as aperture material (a film side outdoor side) of a building, the problem was in endurance. [of hydrophilic maintenance nature]
[0029] (Example 3 of a comparison) About the glass plate with a titanium oxide coat of an example 2, reheat processing was carried out at 700 degrees C. As a result of the approach of showing the obtained glass with the photocatalyst film above estimating, as shown in Table 1 A sample carries out 15g spray of the same coating liquid 1 as the example (example 4 of a comparison) 1 which had a problem in photocatalyst activity being small, and being as large as about 49 degrees, and using 8 degrees and activity as aperture material (a film side outdoor side) of a building at endurance. [of hydrophilic maintenance nature] It was made the pyrolysis on the glass plate and the uniform titanium oxide coat was obtained. The refractive index of the

obtained film was 2.32 and thickness was 30nm. The light reflection factor was 22.0% and solar reflectance was 17.3%. Next, reheat processing of the glass plate with a titanium oxide coat was carried out like the example 1.
[0030]
[Effect of the Invention] As mentioned above, according to the manufacture approach of the multifunctional photocatalyst coat covering glass of this invention It is what offers the multifunctional photocatalyst film covering glass which had the improvement in visibility by the antifouling property and the hydrophilic property into which the contamination organic substance which is made to discover a photocatalyst activity function and adheres to a glass substrate front face is made to disassemble effectively, without spoiling the heat ray reflex function and endurance which are equipped conventionally. Since it has endurance sufficient also by the operating environment which requires endurance which uses the photocatalyst film for an outdoor side, such as a windowpane of a building, and a windowpane for cars, a hydrophilic property, antifouling property by the photocatalyst, etc., it is especially suitable.

[Translation done.]